SYNTHESIS AND REACTIONS OF 2-CYANO-1,3-BUTADIENE

BY

NEAL ORIN BRACE

B.A., University of Minnesota, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1948

URBANA, ILLINOIS

1948

SYNTHESIS AND REACTIONS OF 2-CYANO-1,3-BUTADIENE

BY

NEAL ORIN BRACE

B.A., University of Minnesota, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1948

URBANA, ILLINOIS

1948

ACKNOWLEDGMENT

The Author wishes to thank Dr. C. S. Marvel for directing this research and for his constant interest and many helpful suggestions.

This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

R. UNIV.
BIBLIOTHEEK
LEIDEN

SYNTHESIS AND REACTIONS OF 2-CYANO-1,3-BUTADIENE

Introduction

The synthesis of 2-cyano-1,3-butadiene was investigated in order to determine the most practicable method of preparation. This compound has been prepared previously by the pyrolysis of 2-cyano-2,3-diacetoxy-butane in rather low yield,[1] and by the pyrolysis of 2-cyano-2-acetoxy-3-butene.[2] This last-mentioned synthesis was studied.

The dimers of acetyl and benzoyl cyanide were obtained as by-products in another reaction and the structure of benzoyl cyanide dimer was investigated. A new reaction of acyl cyanides with aromatic aldehydes was discovered.

The dimerization of 2-cyano-1,3-butadiene was observed, and the structure of the dimer elucidated.

Discussion

2-Cyano-2-acetoxy-3-butene was prepared from methyl vinyl ketone by the 1,2-addition of hydrogen cyanide[3] and acetylation.[2] Pyrolysis of this compound gave 27 per cent yield of 2-cyano-1,3-butadiene, but the main product of the reaction was an acetate ester isomeric with the starting material, and pyrolysis of this new ester gave no more 2-cyano-1,3-butadiene.

Proof of the structure of the isomeric ester was obtained by hydrogenation to a saturated derivative and saponification of the cyano-ester to α-methyl-butyrolactone. Thus an allyl-type rearrangement had occured during the pyrolysis, with the acetoxy group underyoiny an α-γ shift, and the double bond moving into conjugation with the cyano group.

The Mannich reaction of allyl cyanide with formaldehyde and dimethylamine hydrochloride could not be successfully

achieved. The cleavage of 3,4-epoxy-1-butene with sodium cyanide and acetic anhydride or benzoyl chloride gave poor yields (30-40 per cent) of the corresponding esters of the cyano-alcohol under all conditions investigated. The dimers of acetyl and benzoyl cyanide were obtained as by-products in these reactions.

While the structure of acetyl cyanide dimer (α-acetoxy-α-methyl-malononitrile is well established,[4] that of benzoyl cyanide dimer previously advanced by Diels and Pillow[5] is inconsistent with the isolation of a diamide and with the infrared spectra of these compounds. The infrared spectra of acetyl and benzoyl cyanide dimers are quite analogous. A more satisfactory structure (α-phenyl-α-benzoyloxy-malononitrile) is suggested for benzoyl cyanide dimer. This structure suggests that the dimer has been formed by the addition of one molecule of benzoyl cyanide to the carbonyl group of another molecule.

It was found that benzoyl cyanide will indeed add to the active carbonyl group of an aromatic aldehyde in the presence of catalytic amounts of aqueous potassium hydroxide. This reaction, which is analogous to the addition of acyl chlorides to aldehydes discovered by Adams and his students some years ago,[6] furnishes a convenient method of converting an aromatic aldehyde to the benzoate of the corresponding cyanohydrin.

2-Cyano-1,3-butadiene dimerizes on standing at 5° in the presence of picric acid to a crystalline solid, whose structure is that of a Diels-Alder condensation product, 1-vinyl-1,4-dicyano-Δ^4-cyclohexene. Proof of the six-membered ring structure was obtained by converting the dimer to a dibasic unsaturated acid, which was dehydrogenated and decarboxylated to *p*-ethyl benzoic acid. The infrared absorption spectrum of the dimer indicates the presence of a conjugated and an unconjugated nitrile group, confirming the structure which would be expected if one molecule of 2-cyano-1,3-butadiene added across the nitrile-activated double bond of

another molecule to give the symmetrical *para* isomer.

A diester of the unsaturated dibasic acid was prepared and its infrared absorption spectrum is analogous to that of the dimer.

BIBLIOGRAPHY

1. Clifford and Long, U. S. Patent 2,328,890; C, A., 38, 1146 (1944).
2. Carter and Johnson, U. S. Patent 2,205,239 to E. I. duPont deNemours and Company, June, 1940.
3. Leupold and Vollman, U. S. Patent 2,166,600 to I. G. Farbenindustrie, June, 1939.
4. Brunner, Montash., 15, 769 (1894); *ibid.*, 13, 835 (1892).
5. Diels and Pillow, Ber., 18, 256 (1908).
6. Adams and Vollweiler, J. Am. Chem. Soc., 40, 1732 (1918); Adams and French, *ibid.*, 43, 651 (1921); Adams and Ulich, *ibid.*, 43, 660 (1921).

VITA

The author was born twenty-six years ago in Osceola, Wisconsin, and attended the public schools there, graduating from high school in May, 1940. After two years of college at the State Teachers College, River Falls, Wisconsin, and somewhat more than a year at the University of Minnesota where he majored in organic chemistry and minored in physics and mathematics, there followed a period of service of thirty-three months in the U. S. Army Air Corps. He was discharged as a First Lieutenant at Camp Grant, Illinois, on March 16, 1946, and immediately began his studies at the Graduate School in the University of Illinois. In the meantime upon recommendation of the Dean of the School of Science, Literature and The Arts in the University of Minnesota he was graduated with the degree of Bachelor of Arts, cum laude, in June of 1946 in absentia. He has been employed as a part time Special Research Assistant on the Government Synthetic Rubber Research Program from March, 1946, to August, 1948.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0261